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DEPARTMENT OF METALLURGY AND MATERIALS SCIENCE

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Final Report on

Synthesis of Hydrogen-Conducting Solid Electrolytes

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Patrick S. Nicholson

Research Associate: M.Z.A. Munshi

Research Assistant: S. Kamenschik

for

Department of Energy, Mines and Resources

(Dr. A.K. Kuriakose - Scientific Authority)

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ABSTRACT

NYS materials were made using spray-dried powders. A series of NYS pellets were ion-exchanged using KCl/NaCl eutectic mixtures to form the precursor KNYS. These samples were H_3O^+ exchanged using constant current. The resultant HNYS pellets were then used to electrolyse steam at 100°C. SEM analysis of the original NYS sinters revealed glassy inclusions and these were hypothesised as the possible cause of electrolyte deterioration sometimes observed during the ion-exchange process.

RESUME

Les NYS materiaux en été produits par pulvérisation à sec de poudre. Une série de NYS pastilles ont subit un echange à fin de former le precurseur KNYS. Ces échantillons furent H_3O^+ échanges utilisant un courant continu. Les echantillons result furent alors utilisé pour electrolyser une vapeur à 100^oC. Des analyses SEM des pastilles NYS (originales) montrérent des inclusions vitreuses et cela fut corrélè à une possible cause de détèrioration observeé parfois durant l'échange ionique.

Objective:

To provide CANMET (Dr. A.K. Kuriakose) with a series of KNYS and HNYS pellets (1.0 cm diameter, 2mm thickness) discs (2.5 cm diameter, 2mm thickness).

Part I Synthesis of Precursor Material, NYS

The chemicals were mixed as follows: one part of 0.1M $Y(NO_3)_3.8H_2O$ (Alfa Product), four parts of 0.1M Na_2SiO_3 "GD" (National Silicates Ltd.) and 0.56 parts of 0.1M Na_2CO_3 (BDH Chemicals). The mixture was cooled in an ice water bath for 2 hours prior to mixing and spraying in a "Buchi" spray-dryer. The solution was stirred constantly to maintain the precipitate in suspension. The inlet and outlet temperatures on the spray-dryer were regulated to 220°C and 102°C respectively. The spray-dried yield of 1 L of 0.1M $Y(NO_3)_3.8H_2O$ was about 50g.

The NYS powder was subsequently calcined at 625°C for 3 1/2 - 4 hours giving a yield of 68-71%. X-ray diffraction of the calcined powder showed it to be an $Na_3YSi_3O_9$ - type structure.

Following calcination, the powder was ball-milled overnight using teflon grinding media. The ball-milled powder was sieved through a #200 nylon sieve and uniaxially pressed into pellets and discs at 3,000 psi. The shapes were enclosed in rubber sleeves and iso-pressed at 30-50kpsi.

Sintering was conducted in a "Pottery Supply House" furnace. The optimum sintering condition was found to be 1135°C for 26 minutes. This condition is necessary to produce single phase sintered NYS with a density >96% theoretical. During sintering, all samples were covered by an atmosphere of their own powder. Density measurements were conducted in iso-butanol and x-ray diffraction was used to determine the phase composition of the sinter.

To meet the materials requirement of CANMET, eight batches of NYS were spray-dried. 63 discs and 31 pellets were sintered and 57 discs and 29 pellets were single phase NYS (Figure 1).

Part II

Ion-Exchange:

The sintered samples were ion-exchanged in a 0.25:0.75/KCl: NaCl eutectic mixture at 800°C for 24 hours to form KNYS. A second ion exchange in 0.5:0.5/KCl: NaCl eutectic mixture at 800°C for a further 24 hours was avoided since earlier samples subjected to this treatment deteriorated.

In spite of the less-vigorous potassium exchange, only 15 discs and 24 pellets survived (Tables I and II). Six discs and six pellets of this KNYS material were forwarded to CANMET.

After potassium exchange, the samples were washed to remove surface chlorides and dried at 200°C. The samples then proceeded to the hydronium ion-exchange and were attached to the exchange unit with RTV Silicone 106 adhesive. H_2 gas enriched with Ar was bubbled just below a Pt foil anode. Another Pt foil acted as the cathode.

Conditions for this process were:

- 0.1M Acetic acid
- a constant current of 1μA was passed through the solid electrolyte at 80°C.
- after 24 hours, the samples were removed, washed and dried at 150°C for 1 hour.

Liquid bright platinum electrodes were painted on the parallel surfaces of the HNYS and it was placed in a vapour phase electrolysis unit at 100°C for 2 hours. 15 volts was applied across the material and the measured current densities were $10mAcm^{-2}$.

Using an established procedure for steam electrolysis the electrolyte was found to break up during removal from the RTV.

To avoid this breakage the exchanged sample was left attached to a section of glass tube. This tube was attached to the hydrolysis unit with a simple tygon tubing collar, facilitating quick removal.

Scanning Electron Microscopy on the original NYS sinter revealed glassy inclusions (Figure 2). It is possible these cause electrolyte deterioration during the ion-exchange processes. The are isolated in pockets and do not seem to change the ceramic conductivity.

TABLE I

Result of NYS Pellets

Code	Thickness (mm)	Density (gr/cm^3)	XRD	KCl/NaCl exch.	H_3O exch	Destination
NYS-7-1	1.946	2.825	Single face	O.K	O.K	CANMET
NYS-7-3	1.900	2.847	"	"	"	"
NYS-7-7	3.563	2.808	"	"	"	"
NYS-8-1	2.817	2.858	"	"	-	"
NYS-8-2	2.556	2.851	"	"	-	"
NYS-8-3	2.669	2.836	"	"	-	"
NYS-8-4	3.145	2.856	"	"	-	"
NYS-9-1	2.923	2.802	"	cracked	-	"
NYS-9-2	3.265	2.834	"	"	-	"
NYS-9-3	3.509	2.808	"	O.K	-	CANMET
NYS-9-4	2.859	2.844	"	"	cracked	"
NYS-9-6	2.601	2.838	"	"	"	"
NYS-10-1	3.528	2.851	"	"	O.K	CANMET
NYS-10-2	3.626	2.848	"	"	"	"
NYS-10-3	3.446	2.860	"	"	"	"
NYS-10-4	3.478	2.857	"	"	"	"
NYS-10-5	3.179	2.869	"	"	"	"
NYS-10-6	3.549	2.854	"	"	"	"
NYS-13-1	2.739	2.788	"	"	"	"
NYS-13-2	3.603	2.791	"	"	"	"
NYS-13-4	2.877	2.802	"	"	"	"
NYS-13-6	3.115	2.805	"	"	"	"

Code	Thickness (mm)	Density (G/cm^3)	XRD	KCl/NaCl exch.	H_3O exch.	Destination
NYS-13-7	3.022	2.814	Single face	O.K	-	CANMET
NYS-6-1	1.54	2.858	"	"	O.K	"
NYS-7-2	1.81	2.853	"	"	-	"
NYS-8-5	1.60	2.854	"	"	O.K	"
NYS-8-6	1.82	2.794	"	"	-	"
NYS-8-10	1.94	2.770	"	"	-	"
NYS-10-3	2.11	2.845	"	"	O.K	"
NYS-10-4	2.31	2.844	"	"	"	cracked
NYS-10-5	2.03	2.790	"	"	-	CANMET
NYS-10-6	2.14	2.852	"	"	-	"
NYS-13-4	2.08	2.808	"	"	O.K	cracked
NYS-13-5	2.10	2.797	"	"	"	"
NYS-8-7	1.73	2.865	"	"	"	"

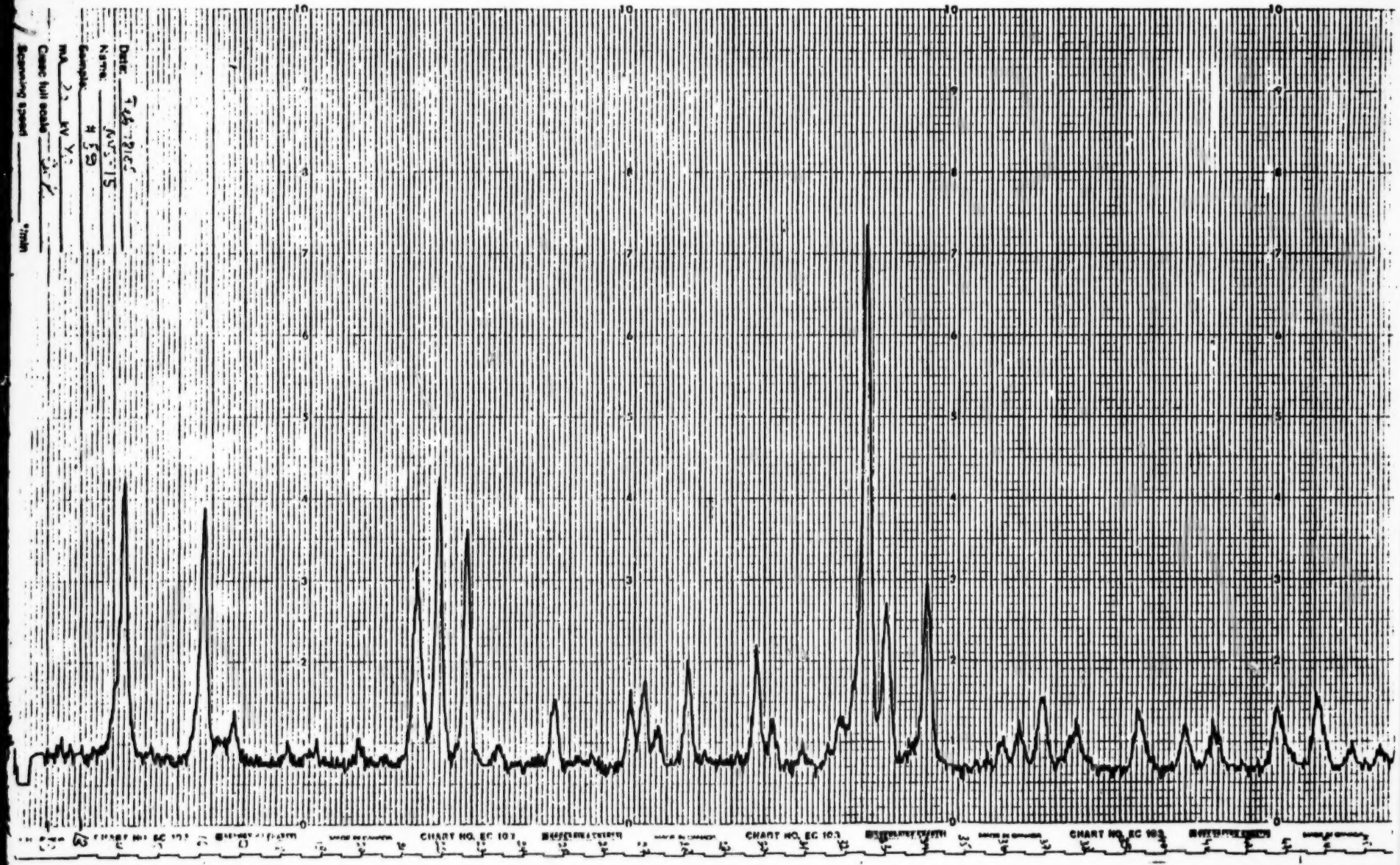

FIGURE 1. TYPICAL X-RAY DIFFRACTOMETER TRACE OF NYS.

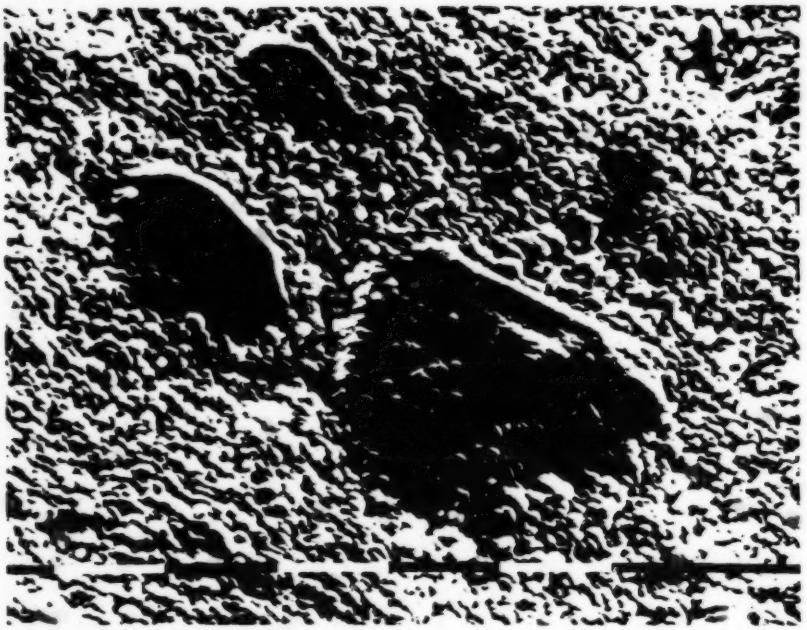

Figure 2: Scanning Electron Microscopy
Photimicrograph Showing
Glassy Phase
1 Marker = 100 μm